Polydopamine coated electrospun poly(vinyldiene fluoride) nanofibrous membrane as separator for lithium-ion batteries

CrossMark

Chengying Cao, Lei Tan, Weiwei Liu, Jiquan Ma, Lei Li*

School of Chemistry and Chemical Engineering, Shanghai Jiaotong University, Shanghai 200240, China

HIGHLIGHTS

- Polydopamine coated electrospun PVDF nanofibrous membranes as separator are prepared.
- PDA coating makes the PVDF surface hydrophilic.
- The battery using the PDA coated separator exhibits better cycling performance.
- The battery using the PDA coated separator shows higher power capability.

ARTICLE INFO

ABSTRACT

In this study, polydopamine (PDA) coated electrospun poly(vinyldiene fluoride) (PVDF) nanofibrous membranes used as separator for lithium-ion batteries are successfully prepared. Their morphology, chemical and electrochemical characterization are investigated. The morphology and porosity measurements of the membranes show that the PDA coating does not harm to the structure of the electrospun PVDF nanofibrous membranes. Due to the PDA coating, it makes the PVDF surface hydrophilic and thus increases the electrolyte uptake and ionic conductivity, resulting in the enhanced performance of batteries. The battery using the PDA coated PVDF nanofibrous separator exhibits better cycling performance and higher power capability than that the battery using the bare PVDF nanofibrous separator. This study underlines that the PDA-coating treatment provides a promising process for the fabrication of advanced electrospun nanofibers separator in the lithium-ion battery applications.

1. Introduction

The importance of lithium-ion batteries (LIBs) has increased in recent years because of rising global energy demand [1,2]. Rechargeable lithium-ion batteries are expected to be used more widely for hybrid and completely electric vehicles as well as for portable electronics. For the construction of these batteries, the development of separator (membrane), which is placed between the positive electrode and the negative electrode to prevent physical contact of the electrodes as well as enabling free ionic transport and isolating electronic flow, is essential [2,3]. Among a number of separators developed so far, thin microporous polyolefin (polyethylene and/or polypropylene) separators have been the most dominant ones for commercial LIBs over the decades [2–6]. These polyolefin separators have many advantageous attributes in terms

of practical application to commercial LIBs, however, due to their poor thermal shrinkage, it is difficult to fully ensure electrical isolation between electrodes. Moreover, their poor wetting capability (hydrophobic surface character) and low porosity (about 40%) hinder the absorption of electrolyte solutions into the microporous membranes. As a consequence, these separators suffer from lower conductivity as compared to pure electrolyte solutions, and fade in both capacity and power capability upon cycling. In addition, the poor wetting capabilities of the polyolefin separators bring addition disadvantages in their manufacturing costs and speeds, especially for large-size batteries, because the electrolytes soaking into separators is one of the slowest step in battery manufacturing processes [7]. Therefore, an advanced separator that can overcome these stringent disadvantages of the polyolefin separators is needed for facilitating the successful development of LIBs applications.

Poly(vinylidene fluoride) (PVDF) is a well-known semi-crystalline thermoplastic polymer with excellent film-forming ability and thermal stability. PVDF porous membranes as separators used in

* Corresponding author. Tel.: +86 21 34202613; fax: +86 21 54742567.
E-mail address: lilei0323@sjtu.edu.cn (L. Li).

LIBs have been widely studied due to their excellent mechanical and thermal properties, good chemical and electrochemical stability [8–10]. In general, the PVDF porous membranes can be prepared by different methods including solution casting, phase inversion and electrospinning. Among them, electrospinning is a predominant and promising technique to produce thin microporous membranes [9,11–17]. Electrospinning is known to be a novel and efficient method to prepare fibrous polymer membranes with fiber diameters ranging from several micrometers down to tens of nanometers. An electrospun nanofibrous membrane has high porosity (up to about 90%), large surface area per unit mass, and a fully interconnected open pore structure. Due to this special structure, the electrolyte can be easily capsulated in the matrix which contributes to a good ion conduction channel and high ionic conductivity of membranes. In recent years, the PVDF nanofibrous membranes prepared by electrospinning technology for LIB applications have been attracted much more attention. Due to higher roughness, however, the contact angle of the PVDF nanofibrous membranes was 130°, which means that these membranes show hydrophobic surface and low surface energy. In order to overcome the poor wetting capabilities of the PVDF nanofibrous membranes, some efforts have been made to modify their surface properties: incorporating inorganic powders such as silica and titanium dioxide [11,12] or blending some hydrophilic polymers like polyacrylonitrile (PAN) and poly(methyl methacrylate) into electrospun PVDF membranes [13,14]. Despite the hydrophilic surfaces are obtained by using these modified methods, it leads to the pores being blocked and porosity decreasing of the PVDF separators, which could lead to lower ionic conductivity, and then directly impair the performance of LIBs.

Herein we report a simple coating method to obtain the hydrophilic surface of electrospun PVDF nanofibrous membranes by using mussel-inspired polydopamine (PDA) (Scheme 1). Polydopamine, one of nature-inspired materials, is a component found in mussel adhesive proteins (MAPs). Mimicking MAPs, dopamine, a biomolecule that contains catechol and amine functional groups, can self-polymerize in weak alkaline aqueous solution and spontaneously deposit PDA films on virtually any surfaces such as bulk substrates and nanostructures [18,19]. Through the PDA coating, the hydrophobic surface of both PTFE and PVDF microfiltration membranes normally used in separation and water purification processes, will be changed to hydrophilic, which were reported to reduce fouling in water purification [20,21]. Moreover, the thickness of PDA coating can be conveniently controlled in a range from that of nearly a monolayer to tens of nanometers. Then such a coating will not cause pore blocking issue. Recently, Choi et al. coated PDA films on commercial polyethylene (PE) separators for

LIBs, and found that the PDA-treating turned PE separators more hydrophilic and improved the performance of LIBs [22,23]. To the best of our knowledge, however, the use of PDA coating on the electrospun nanofibrous membranes for LIBs has never been reported.
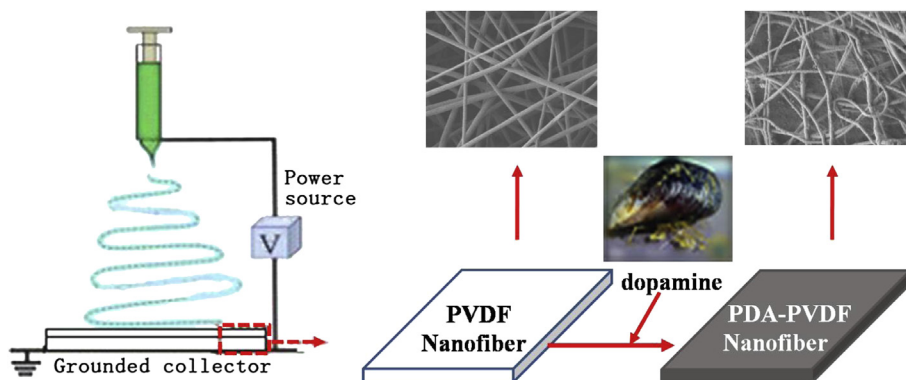
2. Experimental

The electrospinning procedures of PVDF nanofibrous membranes were similar to those described in the previous report [9]. The homogeneous PVDF (13 wt%) electrospinning solution was prepared by dissolving PVDF powder in an *N,N*-dimethylacetamide (DMAC) and acetone (7:3, *wt:wt*) mixed solution. A syringe pump (KD Scientific, Model 200) was used to supply a constant flow rate of 0.4 ml h^{-1} during electrospinning. A voltage of 15 kV was applied draw the nanofibers from the electrospinning solution. The distance between the needle (OD 0.89 mm, ID 0.60 mm) and the aluminum foil collector was 13 cm. The electrospinning process was conducted at ambient temperature in a 25–35% RH atmosphere. The PVDF nanofibrous membranes with a thickness of 30 μm were obtained and dried at room temperature for 24 h, then annealed at 120 °C for 0.5 h to enhance their mechanical strength.

For the PDA coating, the electrospun PVDF membranes were immersed in a Tris–HCl buffer solution of 3,4-dihydroxy phenethylamine (dopamine, 10 mM, pH 8.5, 100 ml) for 24 h at room temperature, then the membranes were taken out, washed with deionized water to remove the residual dopamine and dark brown polydopamine particles. After that, the resulting membranes were dried at 40 °C.

The chemical composition for the membranes was analyzed by Fourier transform infrared spectroscopy (ATR-FTIR, Spectrum 100, Perkin Elmer, Inc., USA), X-ray photoelectron spectroscopy (XPS) using a RBD upgraded AXIS ULTRA DLD system with Mg Kα radiation ($h\gamma = 1253.6$ eV). The morphologies of the membranes were measured by field emission scanning electron microscopy (FESEM, JEOL Ltd., Japan). The porosity of the membranes was determined by a gravimetric method [27]. The surface wetting characteristics of the membranes, water contact angle measurements were carried out by using a contact angle measuring system (SL200C, USA KINO Industry) at room temperature. Ionic conductivity of the membranes at room temperature was determined with two electrodes AC impedance method by using Autolab PGSTAT302 electrochemical test system (Eco Chemie, the Netherlands) over a frequency range of 10^{-2}–10^6 Hz.

Cyclic voltammetry was carried out on Autolab PGSTAT302 electrochemical test system (Eco Chemie, Netherlands) with lithium foil as both the counter and reference electrodes and

Scheme 1. Schematic illustration of the mussel-inspired polydopamine coated PVDF nanofibrous membranes. Dopamine self-polymerizes in the aqueous solution at pH 8.5 and the resultant polydopamine coated surface becomes hydrophilic.

stainless steel as the working electrode. The experiments were performed with sweep rate of 10 mV s^{-1}. All the test cells were assembled and sealed in the glove box.

Battery-grade ethylene carbonate (EC), dimethyl carbonate (DMC) and $LiPF_6$ were purchased from Shenzhen Capchem Chemicals Co., Ltd., China, and used without further purification. The electrolyte of 1 M $LiPF_6$ in a 1:1 (*wt:wt*) EC/DMC was prepared in an argon-filled glove box, in which oxygen and water content were less than 1 ppm.

$LiMn_2O_4$ cathode materials were purchased from Hunan Reshine New Material Co., Ltd., China. The $LiMn_2O_4$ electrodes were prepared by mixing the $LiMn_2O_4$ powder (90 wt%), carbon black (5 wt%) and PVDF (5 wt%) in *N*-methylpyrrolidone (NMP) solvent. The mixed slurry was coated onto aluminum foil and dried at 120 °C for 2 h. The electrode disks (1.5386 cm^2) were then punched out of the coated foil sheets and weighted. $LiMn_2O_4$/Li half cells were fabricated with 2016-coin type cells in the argon-filled glove box using the electrospun PVDF with and without PDA coating membranes as separators. Before the battery assembly, both the membranes were soaked in the electrolyte, 1 M $LiPF_6$ in a 1:1 (*wt:wt*) EC/DMC, for 1 h under an argon atmosphere. The charge–discharge performance of the cells was tested on Land CT2001A tester (Wuhan, China) at the constant current mode over the range of 3.0–4.5 V.

3. Results and discussion

The PVDF nanofibrous membranes were prepared by electrospinning PVDF solution in an acetone/*N,N*-dimethyl acetamine (DMAC, 3:7 *wt:wt*) mixture following previously reported literature [18,22]. The PDA coating on the PVDF nanofibrous membranes was carried out in 10 mM tris–HCl (pH = 8.5) buffer aqueous solution at room temperature. After the PDA coating, the color of the PVDF nanofibrous membranes changed from white to black–brown (Fig. 1a). Fig. 1b showed a typical scanning electron microscopy (SEM) image of originally prepared electrospun PVDF nanofibrous membranes. The nanofibers with smooth surface were randomly distributed in the membranes with diameter of about 400–500 nm.
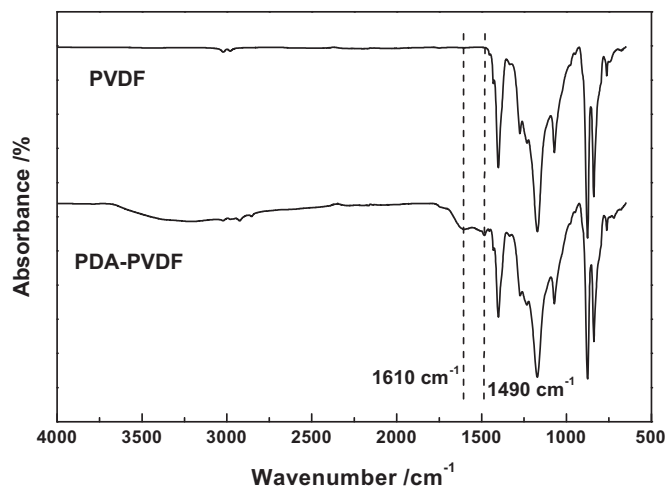

Fig. 2. ATR-FTIR spectra of the PVDF nanofibrous membranes without (PVDF) and with the polydopamine coating (PDA-PVDF).

After the PDA coating, the interconnected open pore structure of the PVDF membranes still remained unmodified (Fig. 1c). Compared with the original PVDF nanofibrous membranes, the nanofibers after the PDA coating showed a relatively rough morphology (Fig. 1c), however, the porosities of the PVDF nanofibrous membranes before and after coating were not changed (about 85%). These results indicate that the PDA coating does not harm to the porosity of the electrospun PVDF nanofibrous membranes.

The PDA coating onto the PVDF nanofibrous membranes was confirmed by Fourier transform infrared spectroscopy (FTIR) and X-ray photoelectron spectroscopy (XPS) measurements. Compared with the original PVDF nanofibrous membranes, some new peaks appeared in the PDA coating membranes (Fig. 2): a broad peak between 3600 cm^{-1} and 3100 cm^{-1} ascribed to N–H/O–H stretching vibration, and the peaks at 1610 cm^{-1} and 1490 cm^{-1} attributed to the overlap of the C=C resonance vibration in the
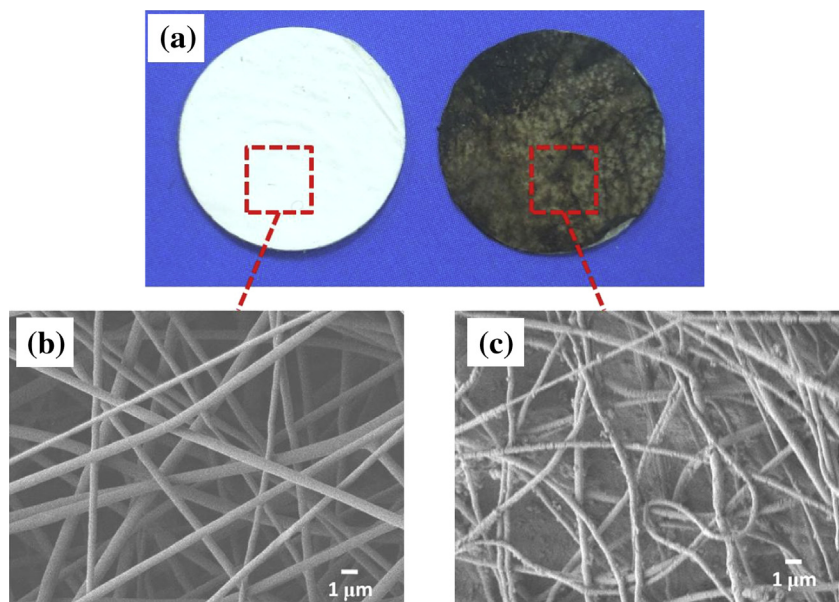

Fig. 1. (a) A photograph of PVDF nanofibrous membranes without (left) and with (right) polydopamine coating. SEM images of the PVDF nanofibrous membranes without (b) and with (c) the polydopamine coating.

aromatic ring and the N−H bending vibration, respectively [20,21]. As the XPS data shown in Fig. 3, only the peaks of C1s and F1s of the original PVDF nanofibrous membranes can be observed. After the PDA coating, two new peaks of N1s and O1s appeared and the peak of F1s was decreased. These results indicated that the polydopamine has been successfully coated on the surface of the electrospun PVDF nanofibrous membranes.

It is well known that the electrospun PVDF nanofibrous membranes exhibit hydrophobic wetting behavior and the contact angle of water is about $125° \pm 2.1°$ (Fig. 4a). Due to the hydrophobic capability of the electrospun PVDF nanofibrous membranes, it can be used for membrane distillation processes [24]. However, it is not suitable for being as separator in LIBs. After the hydrophilic PDA modification, the contact angle of water decreased to $80° \pm 2.5°$ (Fig. 4b), which means that the PDA-coated PVDF nanofibrous membranes have better wetting capability than that of the original PVDF nanofibrous membranes. In addition, the wetting capability of electrolyte solvents on the membranes was quantificationally tested by uptake amount of liquid electrolyte (1 M $LiPF_6$ in EC:DMC = 1:1, wt:wt). As expected, the uptake amount increased from 816 wt% ± 2.1 wt% to 1160 wt% ± 2.1 wt% with the PDA coating. It is well known that the ionic conductivity is directly depended on the uptake amounts of liquid electrolyte in the separators. Then the ionic conductivity increased from 0.683 mS cm^{-1} to 0.962 mS cm^{-1} after the PDA coating. The increased ionic conductivity is attributed to the enhanced electrolyte uptake, which allows a larger number of ionically conducting pathways through the separator pores [22,25].

For practical battery applications, it is important to investigate the electrochemical stability of the separators within the operation voltage of the battery system. The electrochemical stability windows of the PVDF nanofibrous membranes with and without the PDA coating were investigated by using cyclic voltammetry as shown in Fig. 5. The cathodic current onset observed at −0.21 V corresponding to the electrochemical deposition of lithium. And the anodic current onset may be associated with the decomposition of the membranes. It can be found that no significant decomposition of any components in both the PVDF nanofibrous membranes takes place between 1 V and 5 V vs. Li/Li$^+$. This result demonstrates that the PDA coated PVDF nanofibrous membranes have good electrochemical stability, which is suitable as separators for LIBs applications.

The effect of the nanofibrous membranes as separators on the electrochemical performance, including charge−discharge
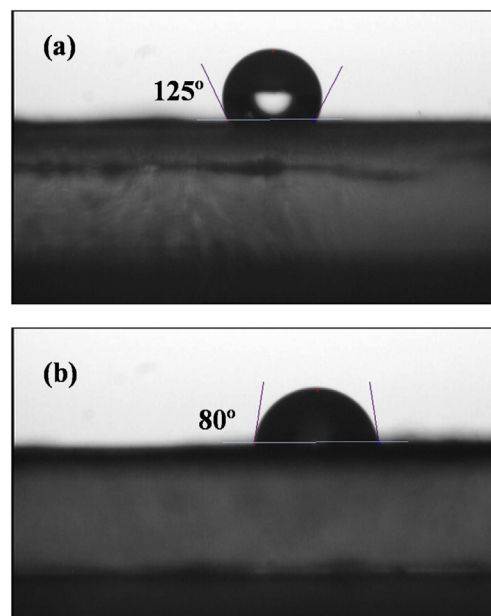

Fig. 4. Contact angle images of the PVDF nanofibrous membranes without (a) and with (b) polydopamine coating.

capacities, cycling performance and C-rate capability, were investigated in LIBs. In our experiments, spinel $LiMn_2O_4$ was used as cathode material, and a lithium metal employed as anode material.

Charge−discharge profiles of the cells at first cycle, which were cycled under a voltage range of 3.0−4.5 V at current density of 0.5 C, were shown in Fig. 6a. Two pseudoplateaus at around 3.9 and 4.1 V that indicate the typical electrochemical behavior of the spinel $LiMn_2O_4$ were observed in both charge and discharge curves [26]. Due to higher electrolyte retention ability and higher ionic conductivity, the performance of the first cycle of the cell using the PDA-PVDF nanofibrous membranes separator (charge capacity: 104.7 mAh g^{-1}, discharge capacity: 104.5 mAh g^{-1}, coulombic efficiency: 99.81%) was better than that of the cell using the PVDF nanofibrous membranes separator (charge capacity: 101.3 mAh g^{-1}, discharge capacity: 101.1 mAh g^{-1}, coulombic efficiency: 99.80%).
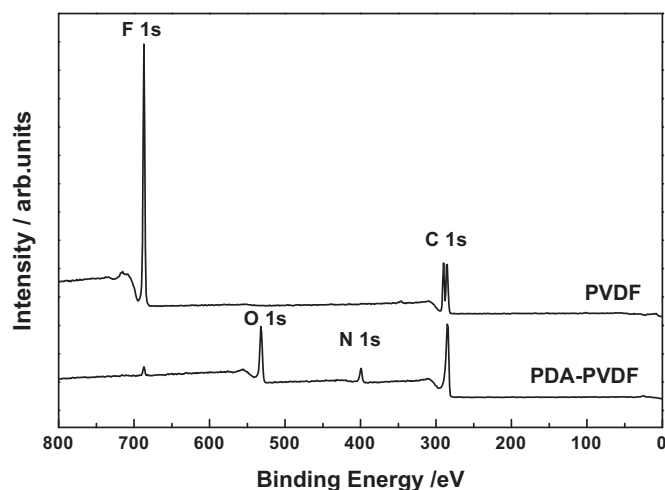

Fig. 3. XPS spectra of the PVDF nanofibrous membranes without and with the polydopamine coating.
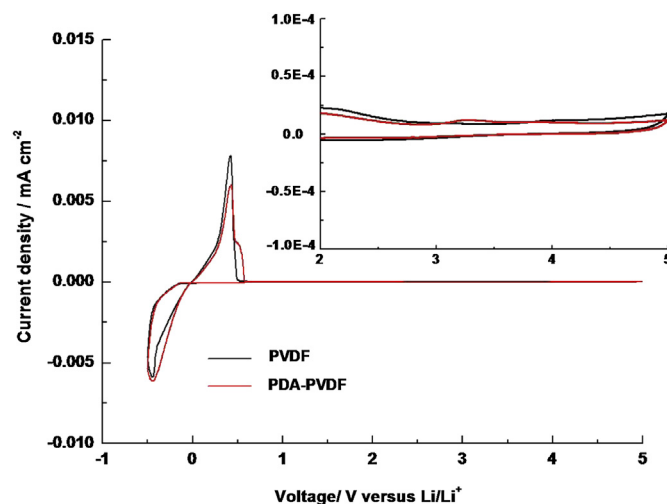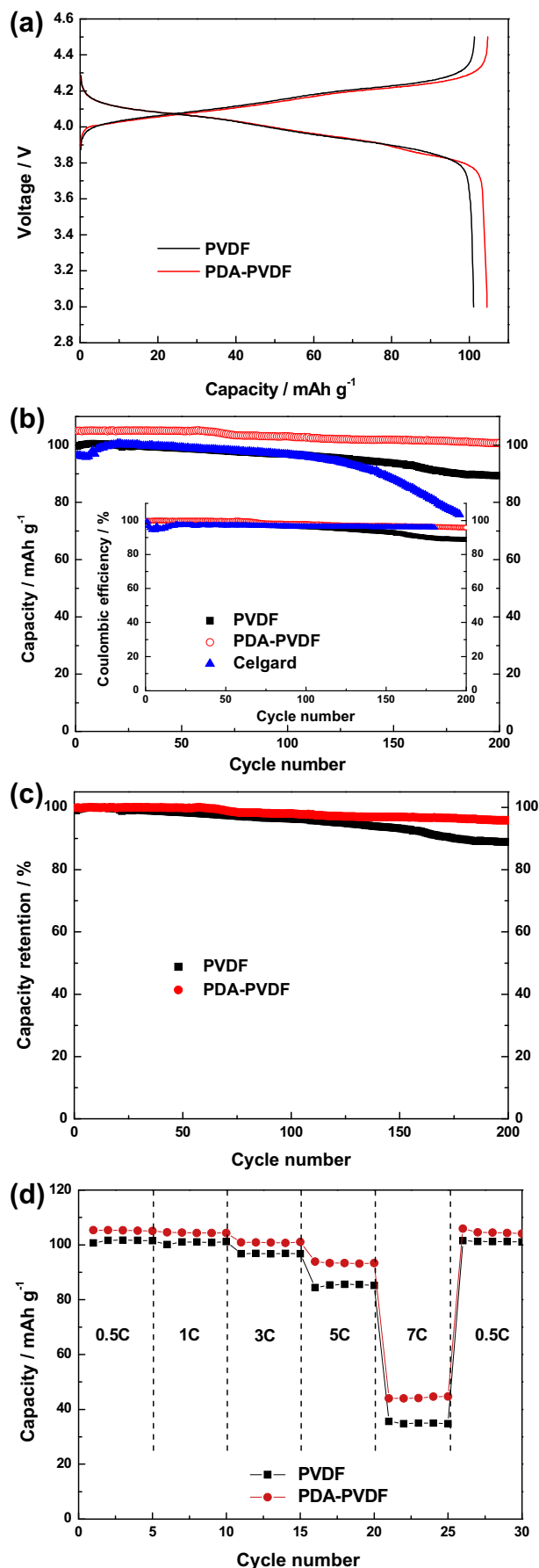

Fig. 5. Cyclic voltammetry curves of the PVDF nanofibrous membranes with stainless steel as working electrode, Li foil as reference and counter electrodes at room temperature (scan rate: 10 mV s^{-1}).

The cycling stability of both nanofibrous membranes separators was evaluated by measuring the discharge capacities of both the cells run at 0.5 C rates under constant current conditions at room temperature. In addition, the cycling performance of the commercial Celgard separator was also measured at the same conditions. It can be found that the cell using the PDA-PVDF nanofibrous membranes separator exhibited very good stable cycling performance (Fig. 6b). The cell with the Celgard separator displayed about 23% capacity loss at the 180th cycle. However, the discharge capacity retention after 200th cycles is found to be 95.8% for the PDA-PVDF separator and 88.9% for the PVDF separator, respectively. In addition, the coulombic efficiency shown in the inset of Fig. 3 (calculated from the discharge/charge capacity) of the cell using the PDA-PVDF separator stays at about 100% after 200th cycles. However, the coulombic efficiency of the cell using the PVDF separator gradually decreases with increasing the cycle numbers, and is about 89.1% after 200th cycles. These results indicate that the PDA coated PVDF nanofibrous membranes is suitable for long-term LIBs operations.

For the rate capability test, the charge current rate was fixed at 0.5 C, and the discharge current rate increased from 0.5 to 7 C in our experiments. Five cycles were performed at each discharge rate, and the test returned to the 0.5 C rate for the last 5 cycles (Fig. 6d). As shown in Fig. 6d, upon the increase of the current rate, the PDA-PVDF separator showed higher capacity retention compared with the retention of the PVDF separator. The improvement in the cycling stability and rate capability of the cell using the PDA-PVDF separator might be attributed to several reasons: first, as mentioned above, the PDA coating causes the PVDF nanofibrous membranes hydrophilic, and thus increases the uptake amount of liquid electrolyte and ionic conductivity. Second, catechol moieties attracted to polydopamine backbones are known to be a critical component of native mussel threads that have extraordinary strong adhesion to versatile substrates [17,18]. Moreover, this mussel inspired adhesion is wet-resistant and thus effective even in liquid environments. Catechol adhesion is expected to cause much strong adhesive interactions between electrodes and the PDA-PVDF nanofibrous membrane separators compared with that between electrodes and the PVDF nanofibrous membrane separators.

Fig. 7 compares the thermal shrinkage of the commercial Celgard separator with the PDA-PVDF separator by measuring the (area-based) dimensional change, where both the separators were exposed to 150 °C for 0.5 h. At this harsh condition, in comparison to the Celgard separator shows the large thermal shrinkage of ~25%, the dimensional change of the PDA-PVDF separator appears to be negligible. These results indicate that the PDA-PVDF separator exhibits good thermal shrinkage.

4. Conclusions

In conclusion, the hydrophilic surface of electrospun PVDF nanofibrous membranes used as separators for lithium-ion battery applications was obtained via surface coating polydopamine. Due to the PDA coating, it not only improves some critical properties of the PVDF nanofiber separators such as electrolyte uptake and ionic conductivity, but also remarkably enhances the LIBs performance including charge–discharge capacities, cycling performance and C-

Fig. 6. Electrochemical characterizations for the Li/separator/LiMn₂O₄ cells using the PVDF nanofibrous membranes with and without polydopamine coating as separators. (a) Charge−discharge profiles at the 1st cycle for the cells with different separators (0.5 C for both charge and discharge). (b) Cycling stability and coulombic efficiency of with different separators. Rate: 0.5 C. (c) Capacity retention of the cells with different separators. (d) Discharge capacity profiles of the cells at various rates. Charge rate: 0.5 C.
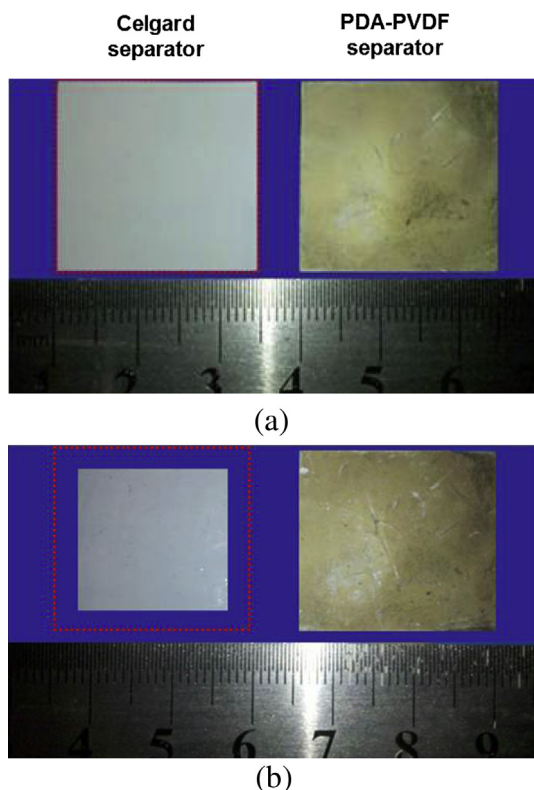
Fig. 7. Thermal shrinkage of the commercial Celgard separator and PDA-PVDF separator (a) at room temperature and (b) after exposure to 150 °C for 0.5 h.

rate capability. We expect that the polydopamine-coating treatment is quite versatile, and will make great progress in the wide application of the electrospun nanofibers used as separators in the LIBs.

Acknowledgments

References

[1] J.M. Tarascon, M. Armand, Nature 414 (2001) 359–367.
[2] B. Scrosati, J. Hassoun, Y.-K. Sun, Energy Environ. Sci. 4 (2011) 3287–3295.
[3] K. Xu, Chem. Rev. 104 (2004) 4303–4417.
[4] G. Venugopal, J. Moore, J. Howard, S. Pendalwar, J. Power Sources 77 (1999) 34–41.
[5] P. Arora, Z.J. Zhang, Chem. Rev. 104 (2004) 4419–4462.
[6] S.S. Zhang, J. Power Sources 164 (2007) 351–364.
[7] C. Daniel, JOM 60 (2008) 43–48.
[8] M. Morita, M. Ishikawa, Y. Matsuda, in: M. Wakihara, O. Yamamoto (Eds.), Lithium Ion Batteries, Wiley-VCH, Weinheim, 1998 (Chapter 7).
[9] S.W. Choi, S.M. Jo, W.S. Lee, Y.-R. Kim, Adv. Mater. 15 (2003) 2027–2032.
[10] S.S. Zhang, K. Xu, D.L. Foster, M.H. Ervin, T.R. Jow, J. Power Sources 125 (2004) 114–118.
[11] P. Raghavan, J.-W. Choi, J.-H. Ahn, G. Cheruvally, G.S. Chauhan, H.-J. Ahn, C. Nah, J. Power Sources 184 (2008) 437–443.
[12] W.-W. Cui, D.-Y. Tang, Z.-L. Gong, J. Power Sources 223 (2013) 206–213.
[13] P. Raghavan, X. Zhao, C. Shin, D.-H. Baek, J.-W. Choi, J. Manuel, M.-Y. Heo, J.-H. Ahn, C. Nah, J. Power Sources 195 (2010) 6088–6094.
[14] X. Li, Q. Cao, X. Wang, S. Jiang, H. Deng, N. Wu, J. Appl. Polym. Sci. 122 (2011) 2616–2620.
[15] C. Yang, Z. Jia, Z. Guan, L. Wang, J. Power Sources 189 (2009) 716–720.
[16] S. Cavaliere, S. Subianto, I. Savych, D.J. Jones, J. Rozière, Energy Environ. Sci. 4 (2011) 4761–4785.
[17] F. Croce, M.L. Focarete, J. Hassoun, I. Meschini, B. Scrosati, Energy Environ. Sci. 4 (2011) 921–927.
[18] H. Lee, S.M. Dellatore, W.M. Miller, P.B. Messersmith, Science 318 (2007) 426–430.
[19] H. Lee, N.F. Scherer, P.B. Messersmith, Proc. Natl. Acad. Sci. U. S. A. 103 (2006) 12999–13003.
[20] B.D. McCloskey, H.B. Park, H. Ju, B.W. Rowe, D.J. Miller, B.D. Freeman, J. Membr. Sci. 413–414 (2012) 82–90.
[21] S. Kasemset, A. Lee, D.J. Miller, B.D. Freeman, M.M. Sharma, J. Membr. Sci. 425–426 (2013) 208–216.
[22] M.-H. Ryou, Y.M. Lee, J.-K. Park, J.W. Choi, Adv. Mater. 23 (2011) 3066–3070.
[23] M.-H. Ryou, D.J. Lee, J.-N. Lee, Y.M. Lee, J.-K. Park, J.W. Choi, Adv. Energy Mater. 2 (2012) 645–650.
[24] Y. Liao, R. Wang, M. Tian, C. Qiu, A.G. Fane, J. Membr. Sci. 425–426 (2013) 30–39.
[25] H.S. Jeong, S.Y. Lee, J. Power Sources 195 (2010) 6716–6722.
[26] H.-W. Lee, P. Muralidharan, R. Ruffo, C.M. Mari, Y. Cui, D.K. Kim, Nano Lett. 10 (2010) 3852–3856.
[27] L. Krishnamoorthy, P.M. Arif, R. Ahmedkhan, J. Mater. Sci. 46 (2011) 2914–2921.